IOP Conf. Series: Materials Science and Engineering **511** (2019) 012019 doi:10.1088/1757-899X/511/1/012019

Mechanical and tribological characteristics of a-C:H:SiO_x films formed by PACVD on titanium alloy VT1-0

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Abstract. This paper is devoted to the study of the mechanical and tribological properties of a-C:H:SiO_x films deposited on a titanium alloy VT1-0 by a plasma chemical deposition method using pulsed bipolar bias voltage. It was shown that after deposition of 2 μm-thick a-C:H:SiO_x film on a titanium alloy VT1-0 sample, the root-mean-square surface roughness R_q measured using atomic force microscopy decreased from 74 to 50 nm compared to the original substrate. The surface hardness H measured using nanoindentation increased from 3.3 to 12.4 GPa with an almost unchanged elasticity modulus E. As a result, the plasticity index (H/E) of titanium samples increased from 0.03 to 0.11, and the plastic deformation resistance (H^3/E^2) increased from 3 to 156 MPa. Deposition of a-C:H:SiO_x film on the titanium alloy VT1-0 surface makes possible to reduce the friction coefficient from 0.3-0.6 to 0.1 and the wear rate from $6 \cdot 10^{-4}$ to $7 \cdot 10^{-6}$ mm^3/Nm.

1. Introduction

Presently, a lot of attention is given to ensuring the durability of metal parts of machines and mechanisms by creating thin-film coatings on their surfaces. The most common coatings are nitride (TiAlN, TiAlCrYN, TiCN, TiN) and carbon-based coatings (DLC) that can reduce friction and wear rates. The addition of SiO_x to DLC allow to reduce internal stresses in DLC films that provides excellent adhesion to many types of substrates and makes it possible to form tens of micrometers thick films [1,2]. On top of that, SiO_x containing DLC (a-C:H:SiO_x) films are characterized by high hardness (10-20 GPa) and elasticity modulus (30-150 GPa) [2-4], low friction coefficient of about 0.02-0.2 [1,5] and wear rate 10^{-5}-10^{-8} $mm^3N^{-1}m^{-1}$ [5,6], high transparency in the visible and near IR wavelength region (~80-85%) [7,8], excellent biocompatibility with human body [1]. Due to the unique properties of a-C:H:SiO_x films, they can be used as wear-resistant anti-friction coatings on parts of internal combustion engines, in MEMS technologies, medicine, industry, lithography [9] and other fields.

The most common method for such films forming is the radio-frequency plasma-assisted chemical vapor deposition (RF PACVD) [5,10,11]. Koshigan *et al.* [1] studied influence of hydrogen and oxygen pressure on tribological characteristics of a-C:H:SiO_x films deposited on silicon wafers. Friction experiments were performed with a linear reciprocating pin-on-flat tribometer, using 52100 steel pins. The authors showed that there are optimal values of gas pressure (H_2 and O_2) in the process of testing at which minimum values of the friction coefficient (0.02±0.01) are observed. Neerinck *et*

al. [12] studied tribological properties of a-C:H:SiO_x films also deposited on silicon substrates. Unlubricated sliding ball-on-disk experiments were performed at room temperature using AISI L3 steel bearing ball. It was shown that in air at a relative humidity (RH) 50% the friction coefficient was 0.04–0.08, while at a relative humidity of 90% and under water, it was lower than 0.15. The wear rate calculated from the profilometry measurement of the wear track area was $2 \cdot 10^{-7}$ $mm^3N^{-1}m^{-1}$ in air of 50% RH and only $3.5 \cdot 10^{-8}$ $mm^3N^{-1}m^{-1}$ under water. Venkatraman *et al.* [13] studied effect of temperature annealing on the tribological properties of a-C:H:SiO_x films deposited on silicon. The wear rate of the annealed films was measured in air at room temperature with a relative humidity of ~35% using a ball-on-disk tribotester with WC ball. The authors showed that with an increase in the annealing temperature in air, graphitization of a-C:H:SiO_x films occurs, as a result of which mechanical and tribological properties deteriorate, in particular, an increase in wear rate from $(1 \div 10) \cdot 10^{-8}$ to $(8 \div 50) \cdot 10^{-7}$ $mm^3N^{-1}m^{-1}$ is observed. Jana *et al.* [14] studied tribological properties of a-C:H:SiO_x films deposited on glass substrates at different relative humidity of the environment. The wear and friction characterization was performed using ball-on-disc tribometer with WC ball. In this paper was shown that increase in relative humidity from 35 to 80% leads to an increase in the friction coefficient from 0.005 to 0.074, while the wear rate is reduced from $9.8 \cdot 10^{-8}$ to $2.7 \cdot 10^{-8}$ $mm^3N^{-1}m^{-1}$ with increasing relative humidity from 35 to 50%. A further increase in relative humidity up to 80% leads to an increase in the wear rate. Bhowmick *et al.* [6] have studied tribological characteristics of a-C:H:SiO_x films deposited on M2 grade tool steel coupons. Pin-on-disk type sliding tests were performed with 319 Al alloy pins. At a room temperature, a-C:H:SiO_x films had friction coefficient of 0.17 and wear rate of $2.86 \cdot 10^{-5}$ $mm^3N^{-1}m^{-1}$. At temperature of 400 °C, the friction coefficient was 0.11, and wear rate was $16.23 \cdot 10^{-5}$ $mm^3N^{-1}m^{-1}$. Jedrzejczak *et al.* [5] have studied tribological characteristics of a-C:H:SiO_x films deposited on cylindrical samples of Ti6Al7Nb alloy in combination with different counterbodies. A ball-on-disc tribometer with AISI 316L and ZrO_2 balls was used. The relative humidity was 30%. In this paper, the authors have shown that a-C:H:SiO_x films have a minimal friction coefficient of 0.04-0.07 at using of both balls. In this case, the wear rate for a-C:H:SiO_x films was from $1.43 \cdot 10^{-7}$ to $3.97 \cdot 10^{-7}$ $mm^3N^{-1}m^{-1}$.

This paper is devoted to the study of the mechanical and tribological properties of a-C:H:SiO_x films deposited on a titanium alloy VT1-0 by plasma chemical deposition method using pulsed bipolar bias voltage applied to substrate. The titanium alloy VT1-0 (Ti content is ~ 99.24-99.7%) is widely used in aircraft and rocket production, medicine and other areas. However, it is known that titanium alloys have the high surface reactivity, low work hardening coefficient, low shear strength, high value of a friction coefficient and a wear rate [15].

2. Materials and Methods

Deposition of a-C:H:SiO_x films was realized on vacuum installation equipped with plasma generator with heated cathode working in mixture of argon and polyphenyl-methylsiloxane (PPMS) vapor. PACVD deposition system has been described in detail in [16]. Vacuum in the chamber to a pressure of 10^{-2} Pa was realized by turbomolecular pump.

Made from titanium alloy VT1-0 samples (size 2×2 cm^2 and thickness 0.4 cm) were used as the substrates. The distance between the plasma generator and the substrate was 100 mm. Before a-C:H:SiO_x films deposition, the substrates were pre-cleaned in argon plasma for 6 minutes. In this case argon pressure in chamber was 0.3 Pa, discharge voltage - 100 V, discharge current - 11 A, magnetic induction in the substrate area - 3 Gs. Bipolar bias voltage with negative pulse amplitude of 1000 V, with frequency of 100 kHz and the positive impulse duration of 4 μs was applied to the substrate during plasma cleaning. After that, a-C:H:SiO_x film was deposited at argon pressure of 0.1 Pa, PPMS flow rate of 95 μl/min, discharge voltage of 140 V, discharge current of 6 A and magnetic induction of 3 Gs. During the film deposition, the negative pulse amplitude of the bipolar bias voltage was reduced to 500 V. Film deposition rate was 3±0.3 μm/h. In [16], we showed that in this deposition regime, the hardest films with the highest sp^3-bonded carbon content are formed on Si substrates.

The deposited a-C:H:SiO_x films were investigated by different characterization techniques. Raman spectroscopy (Centaur U HR complex) with 532 nm Ar laser (beam cross-section of 50 μm) was used for recording of spectra. These spectra were obtained in a spectral range of 800–1800 cm^{-1} with a resolution better than 1.5 cm^{-1}. From the Raman spectra it is possible to obtain information about the carbon bonds in the film. For this, the spectra were divided into Gaussians and the position, width, and intensity of the *D* and *G* Raman peaks were determined. Hardness (*H*) and coefficient of elasticity (*E*) of the a-C:H:SiO_x films were determined by NanoTest 600 device (MicroMaterials, Great Britain) at 2 mN load by Oliver–Pharr method [17]. The surface morphology of the samples was studied by atomic force microscopy using AFM Solver P47 (NT-MDT, Russia) microscope. The friction coefficient was determined using the THT-S- AX0000 (CSM Instruments, Switzerland) tribometer in the "ball on disk" geometry. A ball with a radius of 3 mm made of VK-6 alloy was used as counterbody. The rotation speed of the disk was 5 cm/s, and rotation frequency was 2 Hz at normal load 5 N. Air temperature was 25 °C during the test, and the relative humidity was 50%. Wear rate was estimated by method described in [18]. The film thickness was measured by a Linnik microinterferometer MII 4 (LOMO, Russia).

3. Results

3.1. Atomic force microscopy results

The surface morphology of the samples was studied on initial substrate made from titanium alloy VT1-0, polished by an abrasive paper, and the same substrate coated by a-C:H:SiO_x film. The surface of initial sample had a granular structure with grains of approximately 100 nm in width and 50- 100 nm in height (figure 1,a). After deposition of a-C:H:SiO_x film with the thickness of 2±0.2 μm, the substrate surface became smoother. Root-mean-square surface roughness R_q decreased from 74 to 50 nm. Table 1 presents samples surface roughness values before and after film deposition. In [19] it was shown that the wear rate of DLC films depends on the substrate surface roughness, and latter is the decisive parameter for the wear resistance of the DLC to external loads.

Table 1. Surface roughness characteristics.

Sample	R_{mean} (nm)	R_{max} (nm)	R_q (nm)	R_a (nm)
Initial substrate	258	461	72	57
Coated substrate	134	412	54	43

R_{mean} – mean peaks height, R_{max} – maximum peaks height, R_q – root-mean-square surface roughness, R_a – arithmetic-mean surface roughness.

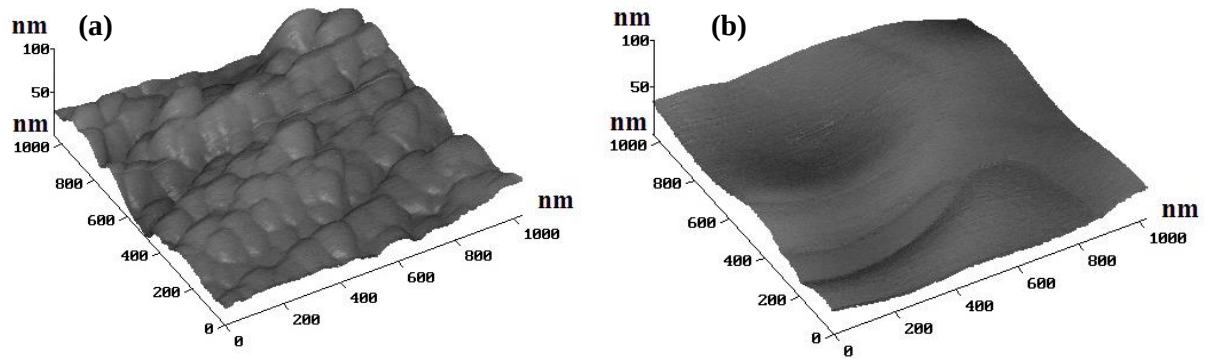

Figure 1. AFM images of initial VT1-0 sample (a) and coated with a-C:H:SiO_x film (b)

3.2. Mechanical characteristics research

The comparison was made between the hardness and the elastic modulus of the initial VT1-0 sample and a sample with a-C:H:SiO_x film (figure 2). It is noticeable that after deposition of a-C:H:SiO_x film, the surface hardness increased from 3.3 to 12.4 GPa. Herewith the elastic modulus of both samples remains almost unchanged – 112.9 and 110.5 GPa. Although hardness is important material property which defines wear resistance, it is considered that the elastic modulus also has an important influence on wear behavior. In particular, the elastic strain to failure, which is related to the ratio of hardness and elastic modulus, is a more suitable parameter for predicting wear resistance [20].

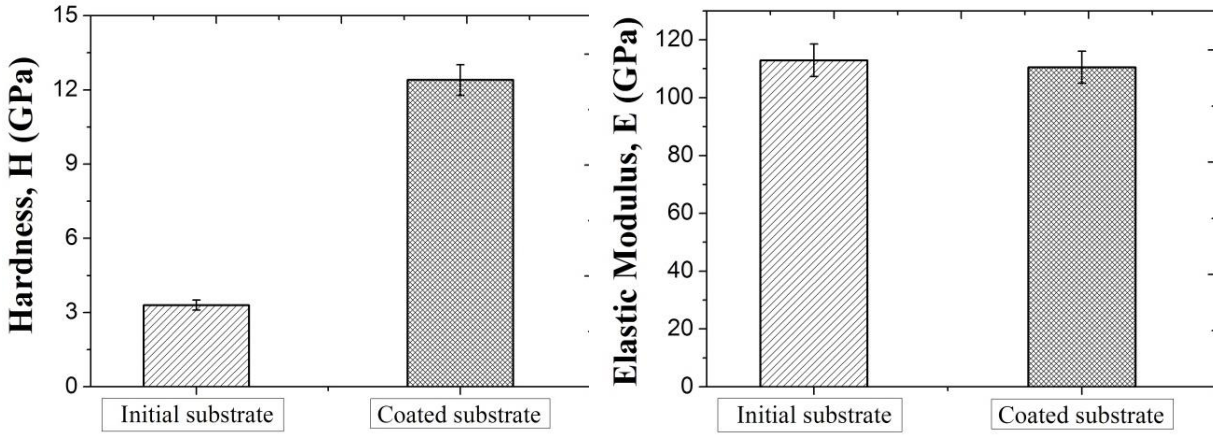

Figure 2. Mechanical characteristics of initial VT1-0 sample and coated with a-C:H:SiO_x film

Since the hardness grew almost 4 times with a practically unchanged elasticity modulus on the sample with a-C:H:SiO_x film, then the elastic-plastic characteristics of the surface (elastic index H/E and plastic resistance H^3/E^2) changed significantly. In particular, elastic index increased from 0.03 to 0.11 and plastic resistance increased from 3 to 156 MPa. The increase in these characteristics indicated an improvement in the wear resistance of the sample surface. Table 2 gives mechanical and elastic-plastic characteristics of the samples surface.

Table 2. Mechanical and elastic-plastic characteristics of the samples surface.

Sample	H (GPa)	E (GPa)	H/E	H^3/E^2 (MPa)
Initial substrate	3.3	112.9	0.03	3
Coated substrate	12.4	110.5	0.11	156

3.3. Tribological properties research

After deposition a-C:H:SiO_x film, the friction coefficient of the sample surface decreased from 0.3-0.6 to 0.1 (figure 3). The initial sample had a friction coefficient that varied in the range from 0.3 to 0.6 and was not stable with time. The reason of the friction scattering was not clear. After film deposition, the friction coefficient not only decreases, but also its oscillations become less pronounced. Except for a short running-in period at the beginning, the sliding on the films soon turns to a stable friction.

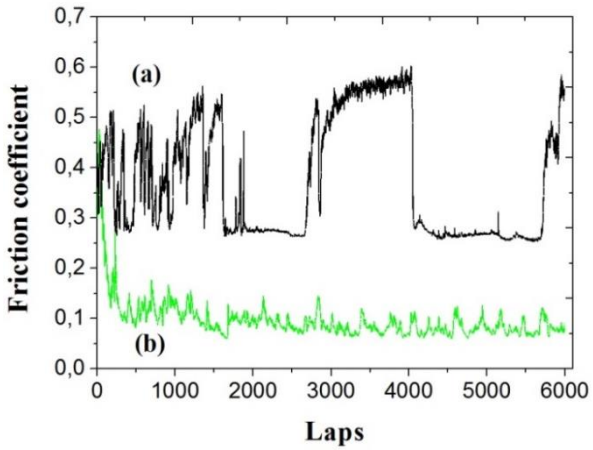

Figure 3. Friction behaviours of initial VT1-0 sample (a) and coated with a-C:H:SiO_x film (b)

Figure 4 show the optical images of wear track of both samples. Wear rate of the sample with a-C:H:SiO_x film, calculated from profile of wear track, decreased from $6 \cdot 10^{-4}$ to $7 \cdot 10^{-6}$ $mm^3/N \cdot m$ in comparison with initial sample. It is clearly seen that the wear track on the VT1-0 sample (figure 4-a) is wider and deeper, while on the sample with the film it is narrower and less deep.

We have previously shown that a-C:H:SiO_x film deposited on the GaAs substrate has higher friction coefficient (0.16) and greater wear rate ($1.3 \cdot 10^{-5}$ $mm^3/N \cdot m$) [21]. Such a difference in film characteristics may be caused by a difference in film deposition conditions, namely another negative pulse amplitude of the substrate bias voltage and Ar pressure during deposition.

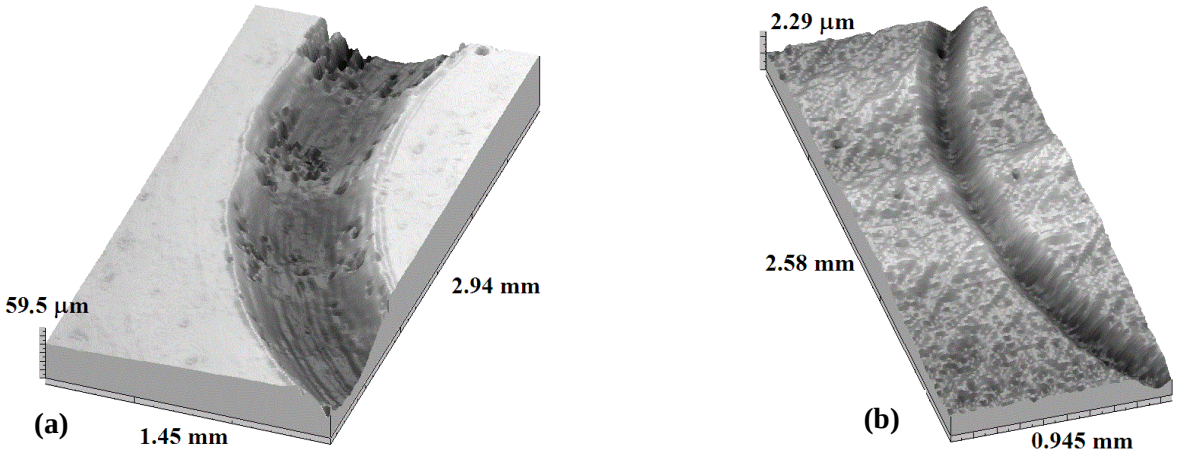

Figure 4. Optical images of wear track of VT1-0 sample (a) and sample with a-C:H:SiO_x film (b)

In paper [22], an influence of electron-ion plasma treatment on tribological properties of a titanium alloy VT1-0 sample was studied. Combined processing in a single vacuum cycle was used for the surface modification. It included nitriding in low-pressure arc plasma and subsequent TiN coating deposition. It was shown that the combined treatment provides the formation of a modified layer which decreases the friction coefficient from 0.4 to 0.3 and the wear rate from $\sim 3 \cdot 10^{-4}$ to $\sim 8 \cdot 10^{-6}$ $mm^3/N \cdot m$. It suggests that a-C:H:SiO_x films are comparable in wear rate to the nitride coating, but significantly exceed it in terms of reducing the friction coefficient.

3.4. Raman spectroscopy

Raman spectroscopy is one of the simplest methods for determining the structure of carbon-based thin films and gives information about the content of sp^3- and sp^2-hybridized carbon atoms in film. Properties of the deposited films depend on the prevalence of one or another hybridization type. Raman spectrum of a-C:H:SiO_x film has wide peak in wavenumber range 1000-1700 cm^{-1} typical for

DLC films (figure 5). This peak was decomposed on two Gaussians, corresponded to D (disordered) and G (graphite) peaks and their position, full width at half-maximum (FWHM), peak intensity ratio I_D/I_G were determined (table 3).

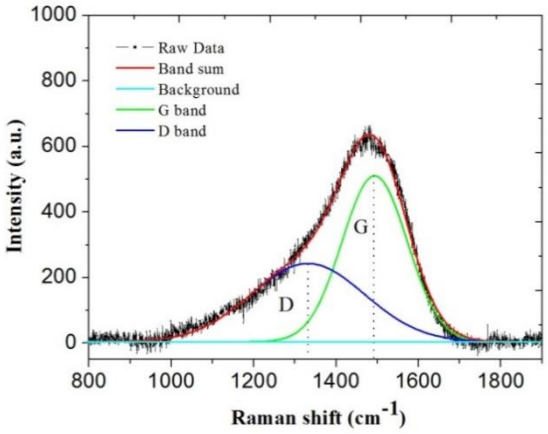

Figure 5. Raman spectrum of a-C:H:SiO_x film deposited on VT1-0 sample

Table 3. Results of analysis of Raman spectrum of a-C:H:SiO_x film.

ω_D (cm^{-1})	Γ_D (cm^{-1})	ω_G (cm^{-1})	Γ_G (cm^{-1})	I_D/I_G
1330	334	1494	189	0.83

ω – peaks position, Γ – full width at half maximum (FWHM), I_D/I_G – intensity ratio.

Conclusions

The results of this study showed that the deposition a-C:H:SiO_x films on the VT1-0 samples allows:

- to increase the surface hardness from 3.3 to 12.4 GPa with a practically unchanged elasticity modulus (110-113 GPa) and, consequently, to increase plasticity index H/E from 0.03 to 0.11 and plastic resistance H^3/E^2 from 3 to 156 MPa;
- to reduce friction coefficient and wear rate by 3.7 times and 85 times, respectively.

Consequently, obtained a-C:H:SiO_x films can be used to increase the durability of products made from titanium alloy VT1-0 in aircraft manufacturing, medicine and other industries.

Acknowledgments

This work was supported by Government task of Institute of High Current Electronics № 0366-2016-0010. The authors are thankful to Tomsk Regional Center for Collective Use of the TSC SB RAS for the provided NanoTest 600 nanoindentator and AFM Solver P47 atomic force microscope.

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